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Molecular Structure and Molecular Vibrations of 1,3,5,7,-Tetramethyl-2,4,6,8,9,10-Hexathiaadamantane

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The molecular structure and vibrations of 1,3,5,7,-tetramethyl-2,4,6,8,9,10-hexathiaadamantane have been determined by a joint computational, gas-phase electron diffraction, and spectroscopic investigation. The geometry and harmonic force field of the molecule was calculated at the Becke3-Lee-Yang-Parr/6-31G* level. Vibrational analysis was performed using FT-IR and FT-Raman spectra recorded in the 4000−150 cm^{-1} range and utilizing Pulay's DFT-based scaled quantum mechanical (SQM) method (DFT: density-functional theory). This SQM method was extended to molecules containing C−S structural motifs. The joint computational and electron diffraction analysis resulted in an equilibrium geometry of T_d symmetry characterized by staggered orientation of the methyl groups with respect to their adjacent C−S bonds. The electron diffraction study yielded the following bond lengths (r_g) and bond angles (with estimated total errors): C−S, 1.820 ± 0.004 Å; C−C, 1.536 ± 0.004 Å; C−H, 1.119 ± 0.005 Å; C−S−C, 102.2 ± 0.2°; H−C−H, 109.9 ± 0.7°. The barrier to methyl rotation was computed to be 17 kJ/mol in good agreement with that estimated from the average methyl torsion (with respect to the staggered form) of 10 ± 3° from the electron diffraction analysis.

Introduction

Adamantane (**1**) is one of the most interesting structures produced by nature. Being the simplest polycyclic saturated hydrocarbon, it possesses a rigid but strain-free ring system composed of three fused chair cyclohexane rings. It represents a fragment of the diamond network saturated by hydrogen atoms. This unique molecule initiated several spectroscopic and structural studies[1−3] extending our knowledge about its properties by now.

One of the questions of adamantane chemistry is the impact of exocyclic and endocyclic substitution in the rest of the molecule. Recently, we reported the influence of fluorination on the adamantane skeleton in perfluoroadamantane.[4] In the present study, our interest is focused on the effects of endocyclic sulfur substitution as in 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathiaadamantane (**2**) (Figure 1). Like **1**, **2** is expected to possess T_d symmetry.

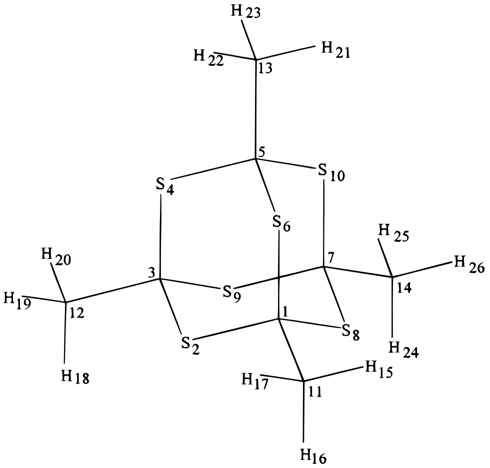

Figure 1. 1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathiaadamantane, **2**. Numbering of atoms.

2 can be prepared by cyclization of thiolacetic acid in the presence of Lewis acids[5] and is known to be an effective inhibitor for age retardation of motor oils.[6] Its crystal structure was investigated by X-ray diffraction confirming the adamantane skeleton.[7] An early infrared and Raman study of the solid combined with a simple normal coordinate analysis gave limited information on the vibrational characteristics of the molecule.[8]

In the present paper, we report a joint structural and vibrational analysis of **2**. To avoid the consequences of possible distortions of the molecular symmetry in the solid phase, our vibrational analysis was based primarily on FT-IR and FT-Raman spectra of CCl_4 solutions. Quantum chemical calculations were carried out at the Becke3-Lee-Yang-Parr/6-31G* level of theory.[9,10] The computed harmonic force field, utilizing

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Pulay's scaled quantum mechanical (SQM) treatment,[11,12] was used for the interpretation of the spectra and to obtain a complete vibrational description of **2**. Supported by the results of the computations and the vibrational analysis, the molecular geometry was determined by gas-phase electron diffraction.

Experimental Section

Synthesis and Purification. Our synthesis is a modification of the procedure of Fredga and Bauer.[5] Thiolacetic acid (53.25 g, 699.6 mmol) was placed into a round-bottom flask along with 300 mL of $CHCl_3$ solvent and 19.49 g of dry $ZnCl_2$ (143.0 mmol). The solution was heated to reflux for 24 h, after which time it was poured into an ice-water bath. Methanol was added carefully until a homogeneous liquid layer was achieved. Off-white colored solids formed during the methanol addition and were collected by suction filtration. The crude solids were washed with distilled water and left to dry under vacuum. (Crude yield: 9.71 g, 36.4%. mp 220−3 °C). 0.9995 g of the crude solids were then sublimed at 135−50 °C under reduced pressure (ca. 5 mmHg) yielding 0.9295 g of pure **2** (93.37%; mp 224−5 °C. ^{13}C NMR: 29.5, 58.5 ppm, $CDCl_3$, 90.6 MHz).

FT-IR and FT-Raman. The FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer using a resolution of 4 cm^{-1} and coaddition of 16 scans. For mid-IR (4000−450 cm^{-1}) measurements, an MCT detector and KBr windows were utilized, for the far-IR (650−150 cm^{-1}), a DTGS detector and polyethylene windows were used. The spectra of the solid were measured using KBr and polyethylene pellets for the mid-IR and far-IR ranges, respectively. For liquid phase measurements, the sample was dissolved in CCl_4 (concentration ca. 0.1 M).

The Raman spectra were measured with a Nicolet Model 950 FT-Raman spectrometer at 2 cm^{-1} resolution using the 1064 nm line of a Nd:YAG laser for excitation (at 100−600 mW output power) and 180° scattering geometry. In general, 512 scans were co-added. Depolarization measurements were performed on the liquid (CCl_4 solution) samples with the same setup using a built-in polarization analyzer set parallel and perpendicular to the electric vector of the exciting laser beam. The solvent spectra were subtracted from those of the solution measured under the same conditions. The Raman spectra communicated here are not corrected for instrument response.

Electron Diffraction. The electron diffraction photographs were taken in a modified EG-100A apparatus[13] with 60 kV electrons, using a membrane nozzle system[14] at about 170 °C. Nozzle to plate distances of about 50 and 19 cm were used. The electron wavelength was calibrated with TlCl powder pattern.[15] Data reduction was carried out as in ref 16. The ranges of intensity data were $1.875 < s < 14.000$ and $8.25 < s < 36.00$ Å^{-1} with data intervals of 0.125 and 0.25 Å^{-1}, respectively.

Computational Details

Calculations were carried out using the 1993 version (G92-DFT) of the GAUSSIAN suite of programs[17] at the Becke3-Lee-Yang-Parr (B3-LYP) level[9,10] with the standard 6-31G* basis set. The normal grid (50,194) was used for numerical integration. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry. The Raman activities were obtained at the HF/6-31G*//HF/6-31G* level of theory.

The vibrational analysis was performed using symmetry coordinates. For the generation of symmetry coordinates of the hexathiaadamantane skeleton, we adopted the method of Cyvin et al.[18] For the methyl groups, local symmetry coordinates[19] were applied. The Cartesian force field was transformed to the symmetry coordinate representation using the program TRA3.[20] Optimization of the scale factors and calculation of the SQM frequencies and mean vibrational amplitudes were done with the program SCALE3.[21,22] For the scaling scheme, Pulay's standard scaling method[23] was used in which the theoretical (unscaled) force constant matrix F was subjected to the congruent transformation $F' = T^{1/2}FT^{1/2}$, where F' is the scaled force constant matrix and T is the diagonal matrix containing the scale factors t_i. The atomic masses used for generation of the G inverse kinetic energy matrix were as follows: H, 1.0078; C, 12.011; S, 32.066 (in amu units).

The quality of the SQM data was assessed by the weighted mean deviation between the experimental and SQM frequencies, where weighting was done by the inverse of the experimental frequency. For characterization of the fundamentals, their total energy distribution (TED)[24] was used.

Vibrational Analysis

The quantum chemical calculations indicated T_d symmetry for **2** characterized by staggered orientation of the methyl groups with respect to their adjacent C−S bonds. Hence its normal vibrations are represented by

$$\Gamma_{T_d} = 5A_1 + A_2 + 6E + 6T_1 + 12T_2$$

the A_1 and E modes being only Raman active and the T_2 modes being both IR and Raman active.

The FT-IR and FT-Raman spectra of **2** (CCl_4 solution) are shown in Figures 2 and 3. Because the A_2 and T_1 modes are inactive in both the Raman and infrared, only limited information can be expected on the molecular vibrations from the experimental spectra. A complete vibrational analysis can only be performed using additional information, e.g., from quantum chemical calculations. Applying the scaled quantum mechanical (SQM) method,[11] a reliable force field can be derived from which the vibrational properties of the molecule can be obtained. Our SQM analysis was based on the B3-LYP/6-31G* computed harmonic force field. Scale factors, developed by Rauhut and Pulay, are available to correct for the deficiencies of this level of theory.[12] These scale factors include those recommended for general use for heavy atom vibrations. The set of model molecules in ref 12, however, did not contain any molecule with C−S structural motif. Thus, as the first step of our SQM analysis, we probed the applicability of these scale factors for the vibrations of sulfur in **2**.

The scale factors used for the different types of vibrations are given in Table 1. We note that these scale factors were originally developed by Rauhut and Pulay for computed harmonic force fields in the natural internal coordinate representation.[12] However, they may be used in our case for symmetry space as well, because the standard scaling method of Pulay[23] is conveniently invariant to transformations which mix internal coordinates with the same scale factor. The SQM treatment using these scale factors[12] (set 1 in Table 1) resulted in a weighted mean deviation of 32.6 cm^{-1} between the experimental and SQM frequencies. Very large deviations (up to 46 cm^{-1}) were found for the CH (overestimated) and CS (underestimated) stretching modes. At the same time, the deformation modes of the CH_3 groups and of the hexathiaadamantane skeleton were well described.

The asymmetric and symmetric stretching fundamentals of CH_3 groups attached to an aliphatic skeleton appear around 2960

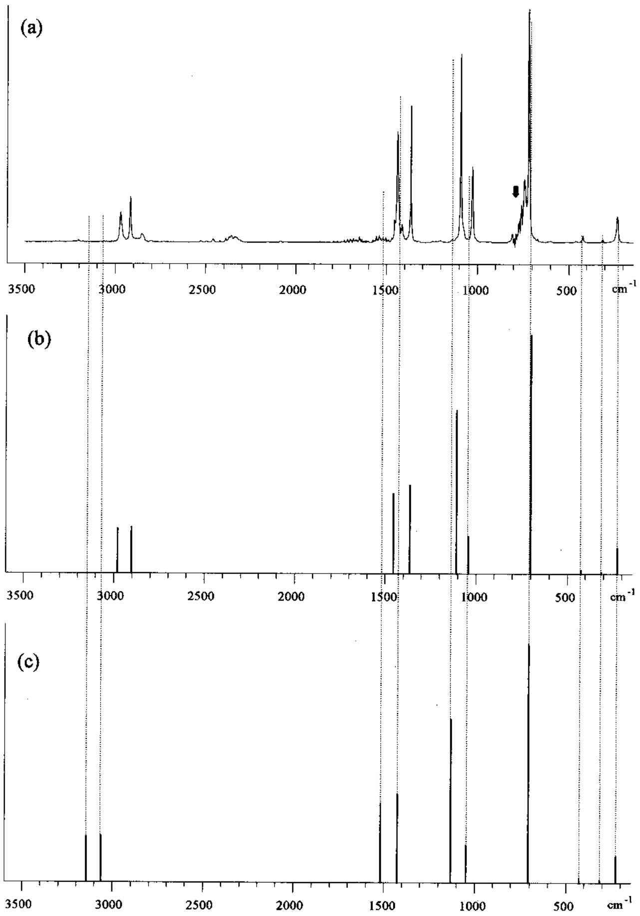

Figure 2. Experimental and calculated IR spectra of **2** (0.1 M CCl_4 solution): (a) experimental, (b) scaled, (c) unscaled (B3-LYP/6-31G*). (↓) indicates strong absorption of the solvent.

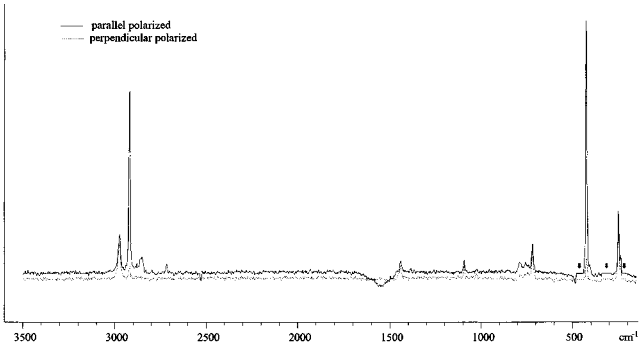

Figure 3. Polarized Raman spectra of **2** (0.1 M CCl_4 solution). (↓) indicates ranges of strong solvent bands.

TABLE 1: Scale Factors for Different Types of Vibrations

vibration	set 1[a]	set 2[b]
skeleton stretching	0.922	1.045
skeleton deformation	0.990	0.990
CH_3 stretching	0.920	0.895
C−C−H bending	0.950	0.950
H−C−H bending	0.915	0.915
C_{skel}−CH_3 stretching	0.922	0.922
C_{skel}−CH_3 bending	0.990	0.990
CH_3 torsion	0.831	0.831

[a] From ref 12. [b] The scale factors for the skeleton and CH_3 stretchings were optimized in the present study.

and 2870 cm^{-1}, respectively.[25] The latter bands are generally weaker than the former. Our experimental results are in agreement with this observation (the corresponding SQM frequencies were 3016 and 2937 cm^{-1}) taking into account the observed Fermi resonance between the symmetric CH_3 stretching fundamental and a combination band near 2865 cm^{-1}. This interaction results in a "blue shift" of the symmetric CH_3 stretching band to 2918 cm^{-1} and in increased intensity (cf. Figure 2 and Table 2). It seems that the error of the B3-LYP/6-31G* level is somewhat different for the stretching vibrations of a methyl group attached to a saturated aliphatic skeleton than for CH stretching of other moieties. (We note that the set of model molecules used by Rauhut and Pulay for the evaluation of the scale factors for CH stretching did not contain any sample with a CH_3 group attached to saturated aliphatic skeleton.) For a better SQM description of these stretching CH_3 modes, a specifically developed scale factor should be used. The similarly poor agreement between the experimental and SQM frequencies for the fundamentals with considerable CS stretching contribution shows the deficiency of the general heavy-atom scale factor for these vibrations.[12]

For a reliable force field to be used for calculating mean vibrational amplitudes in the electron diffraction analysis (vide infra), the scale factors of the above two vibrations were optimized in this study based on the vibrational spectra of **2**. The final set of scale factors is given as set 2 in Table 1. Using set 2, the weighted mean deviation decreased to 7.5 cm^{-1}. A comparison of the experimental and calculated infrared spectra is shown in Figure 2. A complete listing of the experimental, theoretical (B3-LYP/6-31G*), and SQM frequencies of the fundamentals with their assignments is provided in Table 2.

All the IR and Raman active (altogether 23) fundamentals were identified in the FT-IR and FT-Raman spectra, and several overtones and combination bands were observed. The assignment was based on the comparison of the SQM frequencies and (the rather qualitative) calculated IR and Raman intensities with the experimental spectra. The assignment of the A_1 modes was further supported by the results of the Raman depolarization measurements. The SQM analysis indicated very close lying fundamentals in some cases. Thus, ν_3 may be hidden by the more intense ν_{10} and/or ν_{26} bands in the Raman spectra. This 1092 cm^{-1} band was found to be depolarized (cf. Figure 3 and Table 2) showing negligible Raman activity of the ν_3 mode. Similarly, ν_9 may be hidden by the more intense ν_{24}, ν_{12} by ν_{30}, ν_{22} by ν_1, ν_{28} by ν_{11}, and ν_{29} by ν_5 in the Raman spectra (cf. Table 2).

The present assignments are at variance with previously reported assignments[8] at several points which may be due to a lack of both depolarization Raman measurements and a reliable force field in the early work. The present improvement concerns combination bands assigned previously as fundamentals and the C_{skel}-CH_3 bending.

Electron Diffraction Structure Analysis

The numbering of atoms in the molecular model is given in Figure 1. The experimental and theoretical molecular intensities are shown in Figure 4 and the corresponding radial distributions in Figure 5. The latter were calculated by using an artificial damping factor $\exp(-0.002s^2)$.

Assuming T_d symmetry for the heavy-atom skeleton and local C_{3v} symmetry for the methyl groups, the molecular geometry can be described by six parameters. Considering that the experimental radial distribution has at least eight distinct features, this structure seems to make a very good case for electron diffraction. This is further facilitated by the computational and vibrational information. The independent geometrical parameters were chosen to be the C−S, C−C, and C−H

TABLE 2: Normal Vibrations[a] (cm^{-1}) of 1,3,5,7-Tetramethyl-2,4,6,8,9,10-Hexathiaadamantane

		experimental				calculated[b]		
		IR		Raman				
no.	species	solution[c]	solid	solution[c]	solid	scaled	unscaled (IR/Raman int.)[d]	characterization (TED)[e]
1	A_1			423 vs, p	423 vs	419	413 (0, 50)	87% ν skel, 10% ν CC
2					559 w	557	563 (0, <1)	67% δ skel, 23% ν CC, 10% ν skel
3				1092[f]	1086[f]	1084	1116 (0, 4)	66% ν CC, 30% δ skel
4					1355 w	1366	1428 (0, 2)	100% δ_s CH_3
5				2918 s, p	2910 vs	2898	3063 (0, 403)	100% ν_s CH_3
6	A_2					273	300 (0, 0)	100% τ CH_3
7	E			234 w	234 m	231	231 (0, <1)	64% δ $C_{skel}-CH_3$, 24% ν skel, 10% δ skel
8				247 s, d	250 s	247	249 (0, 9)	84% δ skel, 16% δ $C_{skel}-CH_3$
9				719[f]	717[f]	716	709 (0, <1)	69% ν skel, 15% r CH_3, 10% δ $C_{skel}-CH_3$
10				1092 w, d[g]	1086 m[g]	1113	1137 (0, 5)	36 % r CH_3, 36% wa CH_3, 10% δ $C_{skel}-CH_3$
11				1440 w, d	1434 m	1455	1519 (0, 53)	91% δ_{as} CH_3
12				2972[f]	2965[f]	2975	3144 (0, 41)	100% ν_{as} CH_3
13	T_1					178	178 (0, 0)	82% δ skel, 15% δ $C_{skel}-CH_3$
14						272	299 (0, 0)	100% τ CH_3
15						680	668 (0, 0)	84% ν skel
16						1069	1095 (0, 0)	40 % r CH_3, 41 % wa CH_3
17						1454	1518 (0, 0)	92% δ_{as} CH_3
18						2974	3144 (0, 0)	100% ν_{as} CH_3
19	T_2	232 s	235 s	234 w	234 m	226	226 (5, <1)	56% δ $C_{skel}-CH_3$, 26% δ skel, 16% ν skel
20		314 w	311 m	314 s, d	317 s	316	316 (<1, 8)	58% δ skel, 22% ν skel, 16% δ $C_{skel}-CH_3$
21		358 w	359 w		360 w	365	367 (0, 0)	77% δ $C_{skel}-CH_3$, 12% δ skel
22		421 m	421 m	423[f]	423[f]	426	426 (1, 2)	70% δ skel, 17% ν skel
23		509 w	507 w		506 w	513	509 (<1, <1)	68% ν skel, 19% δ skel
24		718 s	716 s	719 m, d	717 m	714	707 (46, 25)	70% ν skel, 10% δ skel, 10% wa CH_3
25		1028 m	1025 s	1024 w	1025 w	1014	1050 (7, 9)	80% ν CC, 14% δ skel
26		1092 s	1087 s	1093 w, d[g]	1086 m[g]	1108	1133 (31, 3)	35% r CH_3, 35% wa CH_3, 11% δ $C_{skel}-CH_3$
27		1366 s	1366 s		1367 w	1364	1427 (17, 3)	100% δ_s CH_3
28		1440 s	1434 s	1440[f]	1434[f]	1455	1518 (15, 1)	92% δ_{as} CH_3
29		2903 m[h]	2899 m[h]	2918[f]	2910[f]	2898	3063 (9, 4)	100% ν_s CH_3
30		2970 m	2965 s	2972 m, d	2965 vs	2975	3144 (8, 143)	100% ν_{as} CH_3

[a] The abbreviations s, m, w, p, d, ν, δ, skel, r, wa mean strong, medium, weak, polarized, depolarized, stretching, deformation, skeleton, rocking, wagging, respectively. [b] Calculated at B3-LYP/6-31G* level. [c] CCl_4-solution (0.1 M) [d] Calculated (B3-LYP/6-31G*) IR intensity in km mol^{-1}. Calculated (HF/6-31G*) Raman activity in Å^4/amu. [e] Total energy distribution (TED),[24] only contributions above 10% are given. [f] Hidden by a more intense band at about the same frequency. [g] Very close lying fundamentals (cf. SQM values and calculated Raman activities). [h] Calculated from the observed frequencies and IR intensity ratio of the Fermi diad.[25]

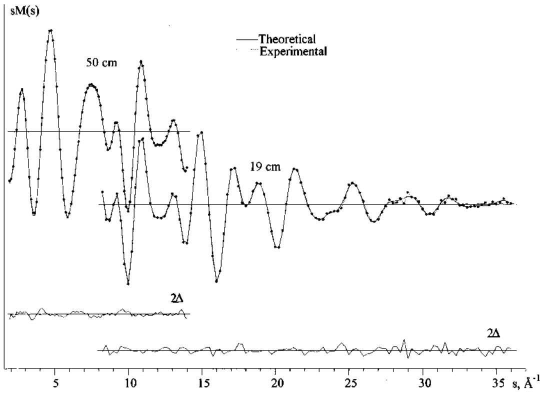

Figure 4. Molecular intensity curves for the two camera distances (Δ = Experimental − Theoretical).

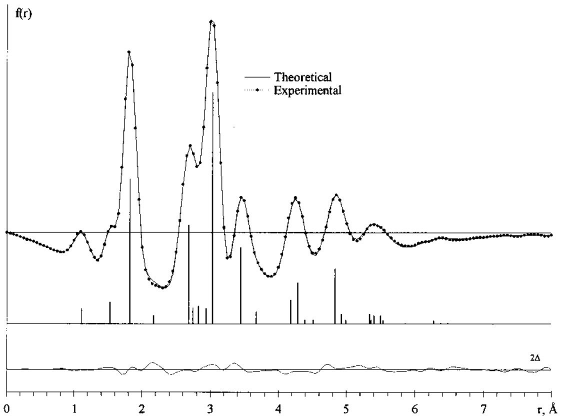

Figure 5. Radial distribution curves (Δ = Experimental − Theoretical).

bond distances, the C−S−C and H−C−H bond angles, and the H−C−C−S angle of torsion. There are 28 nonbonded distances of types C···C, S···S, H···H, C···S, C···H, and S···H.

The least-squares method was applied to the molecular intensities, using a modified version of the program by Andersen et al.[26] Due to emulsion defects on one side of the outer region of the 19 cm plates, the optical density distribution was collected from one side of these plates only in the interval of $s > 27$ Å^{-1}. We used an exponential weight function in this s area, $W(s) = \exp[-0.05(s - 27)^2]$. A total of 31 amplitudes of vibration were refined in 10 groups; the differences between the amplitudes of vibration within a group were fixed. The amplitudes from the SQM analysis obtained by using the scale factors set 2 (cf. Table 1) facilitated the compilation of initial sets of parameters for the refinements. One of the C···H and four of the H···H vibrational amplitudes were assumed at the scaled calculated values throughout the refinements (cf. Table 4).

Only four elements of the correlation matrix of the parameters exceeded 0.5 in absolute value; they are given in Table 3. The results of the least-squares refinements are given in Table 4. The R-factor was 2.7% for the 50 cm data, 5.7% for the 19 cm data, and the total R-factor was 3.7%. The experimentally determined r_g bond lengths and angles and computed principal geometrical parameters are compiled in Table 5. Generally, the r_g bond distances should be larger than the r_e values,[27]

TABLE 3: Elements of the Correlation Matrix Exceeding 0.5 in Absolute Value

i	*j*	ρ_{ji}
$H_{15}-C_{11}-C_1-S_2$	$C_1-S_2-C_3$	0.522
$l(S_2-S_4)$	$l(C_1-S_2)$	0.582
scale2[a]	$l(C_1-S_2)$	0.741
scale2[a]	$l(S_2-S_4)$	0.720

[a] Scale factor for 19-cm data set.

TABLE 4: Molecular Parameters of 2 from Electron Diffraction Least-Squares Refinement (angstroms, degrees)[a]

atomic pair	multiplicity	r_a	*l*	coupling scheme[b]
C−S	12	1.8184(3)	0.060(1)	I
C−S−C		102.2(1)		
C−C	4	1.534(1)	0.050(2)	II
C−H	12	1.114(4)	0.077(4)	III
H−C−H		109.9(5)		
H−C−C−S		50(2)		
$S_2\cdots S_{10}$	3	4.2848(6)	0.090(2)	IV
$S_2\cdots S_4$	12	3.0298(5)	0.082(1)	V
$S_2\cdots C_5$	12	3.4473(7)	0.092(1)	VI
$S_2\cdots C_{11}$	12	2.6803(9)	0.089(1)	VII
$S_2\cdots C_{13}$	12	4.832(1)	0.109(2)	VIII
$S_2\cdots H_{15}$	12	2.75(2)	0.197	VII
$S_2\cdots H_{16}$	12	2.94(2)	0.198	V
$S_2\cdots H_{17}$	12	3.679(4)	0.111(6)	IX
$S_2\cdots H_{21}$	12	5.50(1)	0.14(1)	X
$S_2\cdots H_{22}$	12	5.40(1)	0.153	X
$S_2\cdots H_{23}$	12	4.924(9)	0.194	VIII
$C_1\cdots C_3$	6	2.831(2)	0.079	V
$C_1\cdots C_{12}$	12	4.179(1)	0.088	IV
$C_1\cdots H_{15}$	12	2.170(6)	0.110[c]	
$C_1\cdots H_{18}$	12	4.51(2)	0.176	IV
$C_1\cdots H_{19}$	12	4.989(6)	0.132	VIII
$C_1\cdots H_{20}$	12	4.40(1)	0.176	IV
$C_{11}\cdots C_{12}$	6	5.336(2)	0.111	X
$C_{11}\cdots H_{18}$	12	5.54(2)	0.215	X
$C_{11}\cdots H_{19}$	12	6.267(5)	0.163	XI
$C_{11}\cdots H_{20}$	12	5.36(2)	0.215	X
$H_{15}\cdots H_{16}$	12	1.824(9)	0.126[c]	
$H_{15}\cdots H_{18}$	6	5.86(5)	0.300	X
$H_{15}\cdots H_{19}$	12	6.47(1)	0.216[c]	
$H_{15}\cdots H_{20}$	12	5.34(2)	0.295	X
$H_{15}\cdots H_{21}$	6	7.14(1)	0.152[c]	
$H_{15}\cdots H_{22}$	12	6.37(2)	0.216[c]	
$H_{15}\cdots H_{24}$	6	5.40(5)	0.218	X

[a] Standard deviations are given in paranthesis as units in the last digit. [b] The groups are indicated within which the amplitudes were refined with constant differences. [c] Mean amplitude from the vibrational (SQM) analysis (not refined).

TABLE 5: Geometrical Parameters of 2 from Electron Diffraction and B3-LYP/6-31G* Calculations

parameter	electron diffraction r_g (Å)/angles (deg)[a]	B3-LYP/6-31G* r_e (Å)/angles (deg)
C−S	1.820 ± 0.004	1.846
C−C	1.536 ± 0.004	1.535
C−H	1.119 ± 0.005	1.095
C−S−C	102.2 ± 0.2	102.3
H−C−H	109.9 ± 0.7	108.9
H−C−C−S[b]	10 ± 3	0.0

[a] Estimated total errors according to ref 36. [b] Deviation from the idealized staggered form.

especially for less rigid bonds. The computed C−S bond length appears to be overestimated. The experimental and computed bond angles are expected to be the same, and there is good agreement between them. The overestimated computed C−S bond length may be the main reason for the considerably underestimated CS stretching vibrational frequencies in the computations, not compensated effectively by the heavy-atom scale factors.[12]

Discussion of the Geometry

The cage bond angles in **2** deviate markedly from the regular tetrahedral angle. The S−C−S angle (112.8 ± 0.2°) in **2** is greater than the $C_S-C_T-C_T$ angle in **1** (109.8 ± 0.5°)[1] while the C−S−C angle (102.2 ± 0.2°) in **2** is much smaller than the $C_T-C_S-C_T$ angle in **1** (108.8 ± 1.0°). The C−S−C angle in **2** being much smaller than the regular tetrahedral angle is consistent with sulfur stereochemistry.[28] The C−S−C angle is 98.1 ± 0.8° in dimethyl sulfide,[29] 97.6 ± 0.8° in thiane,[30] 98.7 ± 0.7° in 1,3-dithiane,[31] and 99.1 ± 0.4° in 1,3,5-trithiane.[32] At 102.2 ± 0.2° of the C−S−C angle in **2**, there seems to be little strain in the skeleton. The C−S−C angle slightly opens with increasing number of sulfur atoms in the rigid six-membered ring skeleton in the thiane series.

The C−S bond distance is 1.820 ± 0.004 Å in **2** and 1.811 ± 0.004 Å in dimethylsulfide,[29] 1.811 ± 0.004 Å in thiane,[30] 1.812 ± 0.003 Å in 1,3-dithiane,[31] and 1.812 ± 0.004 Å in 1,3,5-trithiane.[32] The bond distance appears slightly larger in **2** than in the thiane series, which may be due to the crowded hexathiaadamantane skeleton as compared with the isolated six-membered rings.

The C−H bond distance in the methyl groups of **2** is 1.119 ± 0.005 Å. It may be compared with the C−H distance in ethane 1.111 ± 0.001 Å[33] and in ethyl methyl sulfide 1.111 ± 0.008 Å.[34] The H−C−H angle is regular tetrahedral within experimental error. This angle in ethane is only 107.4 ± 0.3°,[33] but it is 109.6 ± 1.4° in ethyl methyl sulfide.[34]

For **1** the relative rigidity of the cage was noted.[1] Curiously there is only one atom pair between **1** and **2** available for direct comparison, viz., $C_1\cdots C_3$ according to the present numbering. The value of the mean vibrational amplitude $l(C_1\cdots C_3)$ is 0.079(1) Å in **2** and is only slightly larger than its counterpart in **1** (0.075 Å).[1] The cage of **2** seems also to be relatively rigid but less so than the cage of **1** itself.

The electron diffraction analysis yielded a 10 ± 3° angle of torsion of the methyl groups from the ideal staggered form. This is an average angle of torsion as a consequence of torsional motion about the C−C axes. Assuming T_d equilibrium symmetry, this average angle of torsion leads to an estimated barrier of methyl rotation of about 17 kJ/mol.[35] The computed value for this barrier was 17 kJ/mol at the B3-LYP/6-31G* level of theory. The numerical coincidence is fortuitous, but the agreement suggests that the assumption of T_d equilibrium geometry in the estimation of the barrier from the average electron diffraction angle of torsion is reasonable.

Conclusions

1. A vibrational and electron diffraction analysis, augmented by B3-LYP/6-31G* calculations, has provided detailed information of the molecular structure of 1,3,5,7-tetramethyl-2,4,6,8,9,-10-hexathiaadamantane.

2. The molecule has T_d equilibrium symmetry with a relatively rigid cage and about 20 kJ/mol barrier to methyl rotation.

3. There is now an improved and more complete assignment of the vibrational spectra than before.

4. Pulay's DFT-based SQM method can be applied to systems with C−S bonds, but a specific scale factor needs to be used for the description of CS stretching vibrations.

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Supporting Information Available: A complete list of symmetry coordinates, unscaled harmonic force field in the symmetry coordinate representation, overtones and combination bands, and total electron diffraction experimental intensities (11 pages). Ordering information is given in any current masthead page.

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